DOCKET NO: 211827US0CONT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF	:
PHILIPPE BOIRE, ET AL.	: EXAMINER: A.T. PIZIALI
SERIAL NO: 09/923,353	:
FILED: AUGUST 8, 2001	: GROUP ART UNIT: 1771

FOR: SUBSTRATE WITH A PHOTOCATALYTIC COATING

DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VA 22313-1450

SIR:

Now comes Bernard Nghiêm who deposes and states that:

1. I hold the degree of "ingénieur" from the "Ecole Centrale de Paris" and I am a graduate of the Université Pierre and Marie Curie, Paris VI, Paris, France. I received my Ph.D. degree in 1998 in the field of "fracture of glass at the nanometric scale."

2. I have been employed by Saint-Gobain Recherche for the past 7 years, first as an "ingénieur" in the department "Transformation and Properties of Glass", and second, since 2001, as the leader of research group in charge of CVD in the department "Thin Coatings on Glass."

3. I have read and am familiar with United States patent 5,721,054, which names Vandiest et al. as inventors (hereinafter referred to as "Vandiest").

4. Vandiest describes the deposition of tin and titanium oxide coatings in accordance with its invention, as follows:

- Liquid tin tetrachloride or liquid titanium tetrachloride is vaporized and introduced in an inert carrier gas (e.g., nitrogen). The resulting mixture, at a temperature of 600°C is introduced in the reaction chamber through one nozzle.
- Water vapour, also at 600°C, is introduced into the reaction chamber through another nozzle.
- Both gas flows contact the substrate surface, where the temperature is between 550°C and 750°C.
- This mixture reacts on the substrate surface to form a tin oxide or titanium oxide coating thereon.
- The deposition tools and methods cited by Vandiest are described in French patent documents FR 2348166 and FR 2648453. The precursor ratio between $SnCl_4$ and water is described in English patent document GB 2026454. See column 5, lines 54-59 of Vandiest
- Vandiest provides no specific description of the gas composition to be used for the deposition of TiO_2 using $TiCl_4$ and water.

After closely examining the deposition procedure described by Vandiest, I believe that, while the conditions given by Vandiest can work well with a mixture of tin tetrachloride and water, this is not the case for titanium tetrachloride and water. On the basis of experiments I performed, I can confirm that for the deposition of titania, the use of the $TiCl_4$ and water ends up creating a nanoparticle powder and does not form a homogeneous coating on the substrate surface. The basis for so concluding is described in detail below.

The reaction of titanium tetrachloride with water is very well-known for creating powder in a fluid flow in order to study the hydrodynamics of the flow. Jensen et al[1] in their review chapter on flow studies within different CVD reactors mentioned the use of this reaction for the visualization of the specific flow patterns as a function of different adimensioned numbers. Because of the very high reactivity of $TiCl_4$ with water, this reaction could occur very rapidly even at ambient temperature. This reactivity increases when the gas temperature becomes higher. When the gases are at 600°C the reaction is instantaneous, and indeed, as mentioned by Vandiest, nanocrystals of TiO_2 anatase are formed, but essentially within the gas phase at the location where the two gas flows are encountering each other and *not on the surface of the substrate*, and the particles deposited on the glass substrate *do not form a real coating, only a "dust" of particles easily removed* with a tissue as discussed above.

Tool described in the patent FR 2648453:

It should be noted that in this patent, the authors mentioned the use of $TiCl_4$ for the deposition of titania but in conjunction with oxygen and not with water. Figure A (extracted from FR 2648453) is a schematic view of the double nozzle tool for the deposition of metal oxides. The main claim of this patent is the use of nozzles with an incident angle of the gas flow on the surface, which is lower than 45° to insure a non turbulent gas flow and the flow of a metal compound underneath the oxygen containing flow (claim 13). If such a configuration (in figure 3) is used with water and titanium tetrachloride, at the intersection region between the 2 flows from the 2 nozzles, nano powder is formed instead of a coating.

[1] Micheal L. Hitmann & Klavs F. Jensen, « Chemical Vapor Deposition principles and applications », pp. 50 to 53, Academic Press limited copyright © 1993.

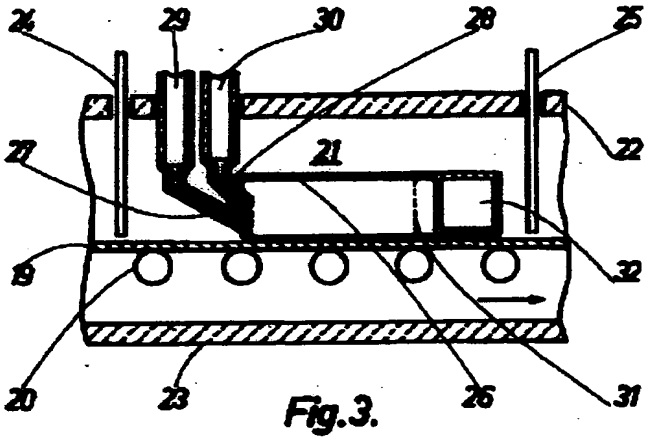

Figure A : scheme of the double nozzle claimed in the patent FR 2648453

Tool described in FR 2648453:

This patent was analysed but concluded to be less relevant because it concerns the use of a single nozzle with a good premixing of the precursors gases before they enter the deposition zone, instead of the double nozzle described by Vandiest.

This patent describes technology for the deposition of SiO_2 from SiH_4 and oxygen. The first claim concerns a very good mixing of both components before the deposition chamber. So if this kind of tool is used with $TiCl_4$ and water instead of SiH_4 and O_2, a nano power should be formed before arriving on the substrate surface.

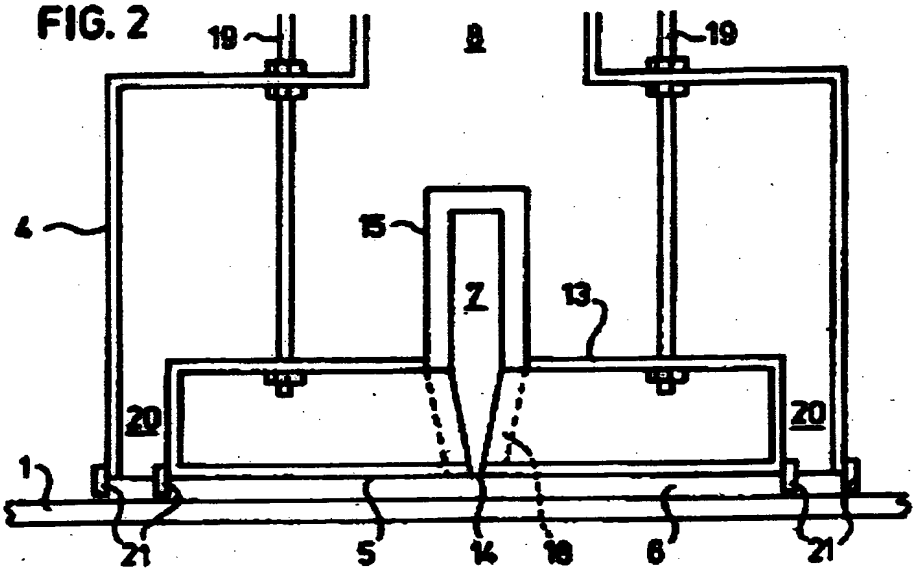

Figure B : Scheme of the nozzle for the deposition of SiO_2 from the patent FR 2648453

Experiments:

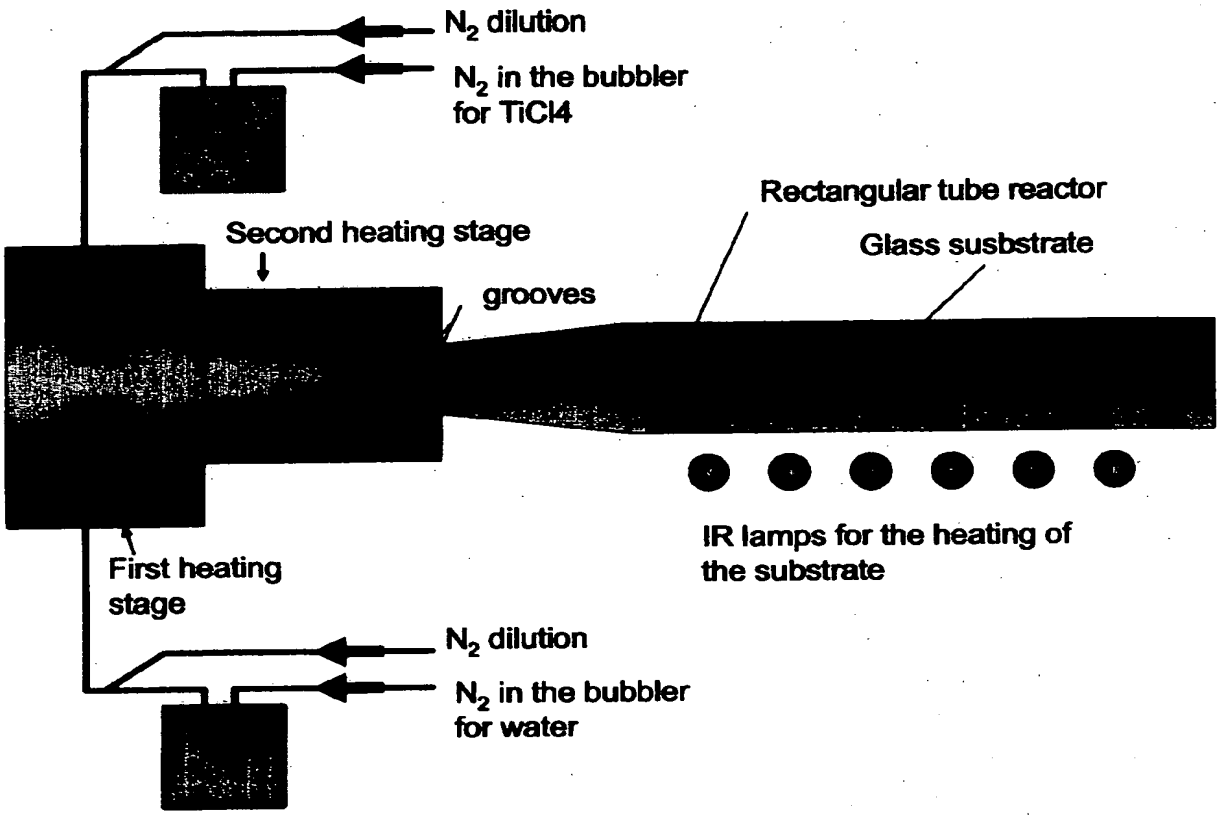

Figure C : schematic view of the CVD reactor

To reproduce the conditions of the deposition and the tool for the gas injection described by Vandiest and FR2648453, we used a CVD reactor with a static substrate as described in figure C. These experiments were conducted by me or under my supervision and control. This reactor is composed of a first furnace where the gases can be heated and a second shorter furnace to complete the heating of the gases. The two precursor gases are

injected into the reaction chamber through two horizontal grooves. The gas flow is parallel to the substrate surface which can be heated by IR lamps to a determined temperature.

Definition of the process parameters:

$TiCl_4$ is vaporized in nitrogen through a classical bubbler system. Nitrogen is injected through liquid $TiCl_4$ which is maintained at a constant temperature $T_{TiCl4\ bubbler}$. The partial pressure at this temperature defines the amount of vapour of $TiCl_4$ that will be carried away by the nitrogen. $N_{2\ TiCl4}$ is the flow rate of nitrogen through the bubbler. $N_{2\ dilution\ TiCl4}$ is the flow rate of added nitrogen gas for the dilution.

The same system is used to inject water vapor in the nitrogen carrier gas. $T_{water\ bubbler}$ is the temperature of the bubbler. $N_{2\ water}$ is the flow rate of nitrogen through the bubbler. $N_{2\ dilution\ water}$ is the flow rate of added nitrogen gas for the dilution.

The gas lines are heated also by heating strings at the temperature $T_{line\ x}$ (X can be $TiCl_4$ or water)

Both gases are separately injected in different tubes surrounded by a first furnace where the contact time is high. $T_{furnace}$ is the temperature of the first furnace

Then the gases pass through a second furnace where the contact time is shorter. $T_{ring\ furnace}$ is the temperature of the second furnace

The substrate is heated up to a determined temperature $T_{substrate}$, using IR lamps.

$t_{deposition}$ is the deposition time

2 types of substrate were used:

- Planilux (air side) which is the commercial soda lime glass produced by Saint Gobain
- Planilux coated with Antelio clear which is a FeO_x CrO_y CoO_z coating

The table below summarizes the parameters we have used for the deposition of titania coating.

Parameters	Substrate : Planilux	Substrate : FeCrCoOx/Planilux
$t_{deposition}$	3 min	3 min
$T_{substrate}$	600°C	600°C
$T_{furnace}$	600°C	600°C
$T_{ring\ furnace}$	650°C	650°C
$T_{line\ water}$	60°C	120°C
$T_{line\ TiCl4}$	50°C	120°C
$T_{TiCl4\ bubbler}$	30°C	30°C
N_2 TiCl4	1 slm	1 slm
N_2 dilution TiCl4	2 slm	2 slm
$T_{water\ bubbler}$	40°C	40°C
N_2 water	2 slm	2 slm
N_2 dilution water	1 slm	1 slm

With the preceding condition water is largely in excess compared to titanium precursor as described in the GB patent noted above.

Results:

With the preceding deposition parameters, we could not deposit any real coating. Instead, we produced a powder, part of which weakly adheres to the surface of the substrate when the experiment was over. This powder can be easily wiped out by a tissue cloth.

Conclusion:

The process parameters described by Vandiest for the deposition of large gap semi conductor like SnO_2 or TiO_2, starting from Ti or Sn tetrachloride with water as oxidant are only valid for the deposition of SnO_2. In the case of TiO_2, our own experiments and several scientific sources have proven clearly that even at low temperature TiO_2 powder is formed when $TiCl_4$ and water is brought into contact, instead of an homogeneous coating on the surface.

4. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

5. Further deponent saith not.

Bernard Nghiêm

14/09/05

Date